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INFRARED TRANSMITTING ANALOGS OF SIALON(U) BATTELLE  
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Infrared Transmitting Analogs of SIALON

by

Peter J. Melling

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## Infrared transmitting analogs of SiAlON

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SiAlON

Abstract

There is a requirement for new materials which are transparent in the 8-12  $\mu\text{m}$  range and have superior thermal shock resistance, mechanical strength, toughness and thermal stability compared to those materials which are presently available. In oxide systems, the SiAlON family of ceramics and glasses is known to have particularly good thermal shock resistance and mechanical properties, thus GeGaSP analogs of the SiAlON ceramics should be a promising system to investigate for new materials. Preliminary results of an experimental study are reported.

Introduction

Typically, materials for infrared (IR) transmitting windows and domes have inadequate combinations of properties; they need to have satisfactory IR transmission to resist environmental degradation and they need to be cost-effective in their fabrication. There are three basic approaches that can be used to fabricate a ceramic: the growth of single crystals, the consolidation of powder to give a polycrystalline ceramic and fabrication as a glass. Single crystals are usually exceedingly difficult to fabricate in sizes large enough to be useful. Ceramics can be prepared in composition ranges where glasses cannot be formed and in fine-grained polycrystalline ceramics careful heat treatments can be used to provide toughening of the final body. Glasses have many advantages over polycrystalline ceramics in other ways, however, Glasses do not usually need to be densified, as they are fully dense as cast; they can be molded or slumped into final shape using simple technology; and, provided they do not phase separate, glasses do not suffer from optical scattering losses due to grain growth.

Oxynitride ceramics in general, and the SiAlON system in particular, are known to have mechanical properties superior to conventional oxide ceramics<sup>(1)</sup>, particularly in terms of hardness and thermal shock resistance. However, because of the position of the absorption bands present in oxide and oxynitride ceramics, they are unsuitable for 8-12  $\mu\text{m}$  transmitting materials. In order to shift the absorption to longer wavelengths, a move to heavier atoms is required. The necessary shift in wavelength should be achieved by using the elements, one period down on the Periodic Table to give the GeGaSP system.

Background

There are no previous reports on work in the GeGaSP system and the only previous work on the Ge-S-P system is that by A.R. Hilton<sup>(2)</sup>, which was performed about 20 years ago. In that work, Hilton studied a series of phase diagrams of chalcogenide glass systems (Table 1). He reported that the glasses in the Ge-S-P system had the highest softening points and among the highest hardnesses of the composition ranges he studied.

Table 1. Highest Softening Points of the Glasses Studied by A.R. Hilton<sup>(2)</sup>

Glass Composition Range	Softening Temperature (C)
Si-Sb-S	280
Si-Sb-Se	270
Si-P-Te	180
Ge-P-S	520
Ge-P-Se	420
Ge-P-Te	380
Si-As-Te	475
Ge-As-Te	270

As part of the study, Hilton investigated the relationship between hardness and softening temperature for a wide range of chalcogenide glasses and found a clear positive correlation<sup>(2)</sup>. The IR spectra of glasses in the Ge-S system show very good transmission up to  $\mu\text{m}$ , but spectra of glasses in the Ge-P-S system have a cutoff at about  $7 \mu\text{m}$ <sup>(2)</sup>. The origin of the band which causes this cutoff is uncertain, but it could arise either from structural rearrangement in the glass or from phosphate or other oxide impurities.

#### Sample Preparation

Two methods are being used in this work to prepare materials for study: one employs a conventional rocking furnace with modifications to make the system explosion-resistant and the other employs a chemical vapor deposition (CVD) system to prepare mixed powders for further processing. The advantages of CVD powder preparation are the potential for reduced contamination and the ability to produce prereacted mixed powders suitable for further processing.

In conventional sealed-tube melting the reactants, as elements, are sealed in a quartz ampoule which is then heated in a furnace. The apparatus we are using is shown in Figure 1; a rocking furnace was chosen to ensure complete mixing of the glass components. A problem with this approach, which is more significant with phosphorus- and sulfur-containing glasses such as those studied in this work than with the more traditional selenides and arsenides, is the generation of high pressures in the ampoule during the melting phase which can lead to explosions. To use the germanium-sulfur system as an example, the reaction between germanium and sulfur goes not to completion until germanium melts at  $935^\circ\text{C}$ . At that temperature, the vapor pressure of sulfur exceeds 10 MPa, so we are using thick-walled (3 mm wall) ampoules with stainless steel pipe containment. In this arrangement, the ampoule is mounted in the pipe before being placed in the furnace and is retained in the pipe during quenching at the end of the run. This system is highly satisfactory and has survived a number of catastrophic failures of the ampoule. If ampoule failure occurs at high temperature, however, it is necessary to replace the pipe, as the vapor generated by the glass melt is very corrosive.

Because of problems associated with preparing glasses from the elements, we are investigating the CVD preparation of mixed powders, which will then be melted conventionally. This should substantially reduce the maximum temperatures required during the melting process and hence reduce the problems associated with high temperatures. To obtain the powders, we react gaseous precursors such as  $\text{GeCl}_4$  vapor and  $\text{PH}_3$  in an HCl flame in a Technier burner. In this apparatus, a flame is burnt in an inert chamber and the powder is collected as soot on the chamber walls. High reaction temperatures and quench rates can be achieved with this method.

#### Ge-Ga-S-P Glasses

Preliminary experiments with melt compositions in the same ratio as compositions in the center of the  $\beta\text{-SiAlON}$  region of the SiAlON phase diagram produced crystalline material that had incompletely melted and batches prepared with excess phosphorus were prone to explosions on cooling, an observation which is consistent with the work in reference (2) where it was found that high phosphorus glass melts were prone to explode.

A glass in the Ge-P-S system which Hilton<sup>(2)</sup> reported to be stable,  $\text{Ge}_{0.4}\text{P}_{0.4}\text{S}_{0.2}$ , was prepared. This glass was reported as being homogeneous, but under the scanning electron microscope a globular structure is observed (Figure 2) which strongly suggests that phase separation is occurring. A differential thermogram (Figure 3), measured under dry nitrogen, shows a glass transition at  $417^\circ\text{C}$ , which is close to the reported softening temperature of  $450^\circ\text{C}$  and a deviation in the baseline at  $450^\circ\text{C}$ , which suggests a second glass transition that could be due to a second phase. X-ray diffraction (XRD) of the glass gives a completely amorphous diffractogram. A Knoop hardness of 346 with a standard deviation of 32 was obtained; this is harder than any of the values obtained by Hilton<sup>(2)</sup> (all samples measured by Hilton were  $<250$ ). Reduction of the sulfur content to give the composition  $\text{Ge}_{0.45}\text{P}_{0.45}\text{S}_{0.1}$  resulted in a polycrystalline metallic looking material with a high electrical conductivity, as did addition of gallium to give the composition  $\text{Ge}_{0.35}\text{Ga}_{0.12}\text{S}_{0.18}\text{P}_{0.35}$ .

To begin investigating the low phosphorus region of the phase diagram, a melt with the composition  $\text{GeGa}_{0.2}\text{S}_{1.5}$  was prepared. This gave a good glass, and the IR transmission spectrum on a sample 2 mm thick is shown in Figure 4. The origin of the absorption band at  $9.5 \mu\text{m}$  is uncertain, but it is probably due to a rearrangement of the structure from that of the  $\text{GeS}_{1.5}$  glass which does not show the band<sup>(2)</sup>. The Knoop hardness, determined with a 100 g load, was 214 with a standard deviation of 14. A differential thermogram given in Figure 5 shows a glass transition at  $308^\circ\text{C}$  and a crystallization at  $420^\circ\text{C}$ .

### Conclusions

Glasses in the GeGaSP system have considerable potential for IR window applications, but that potential needs to be explored in considerably more detail before a judgement can be made. Gallium can be incorporated into germanium sulfide compositions and a stable glass prepared, but that this incorporation results in a deleterious absorption band at  $9.5\ \mu\text{m}$ . The origins of this band need to be investigated to determine whether it can be removed by suitable purification procedures or compositional variations.

### Acknowledgements

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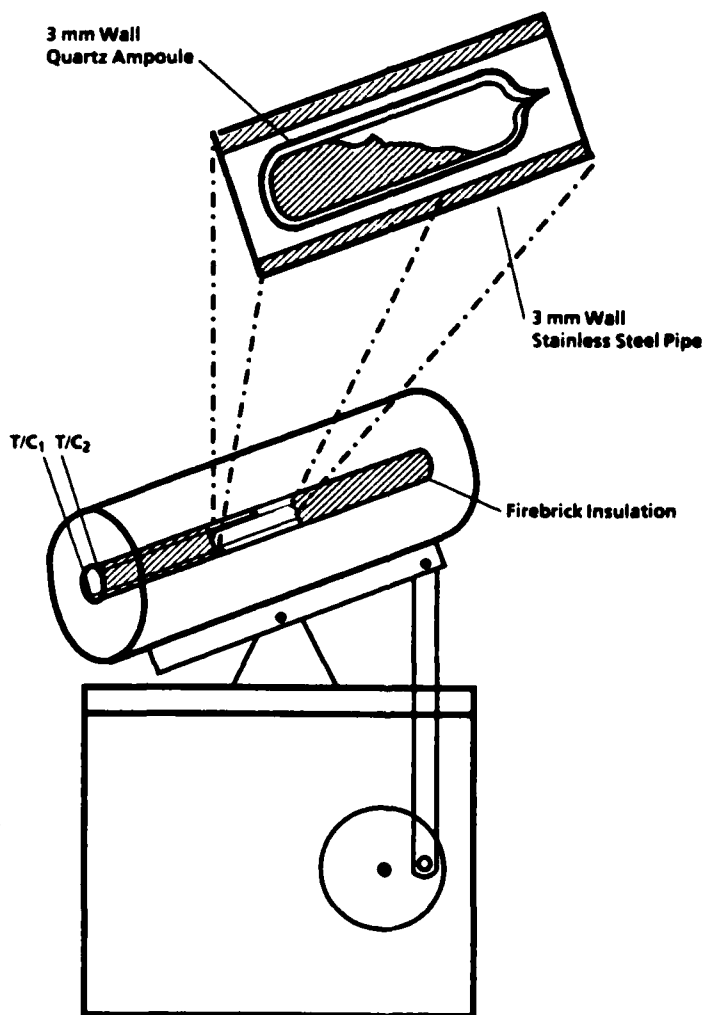
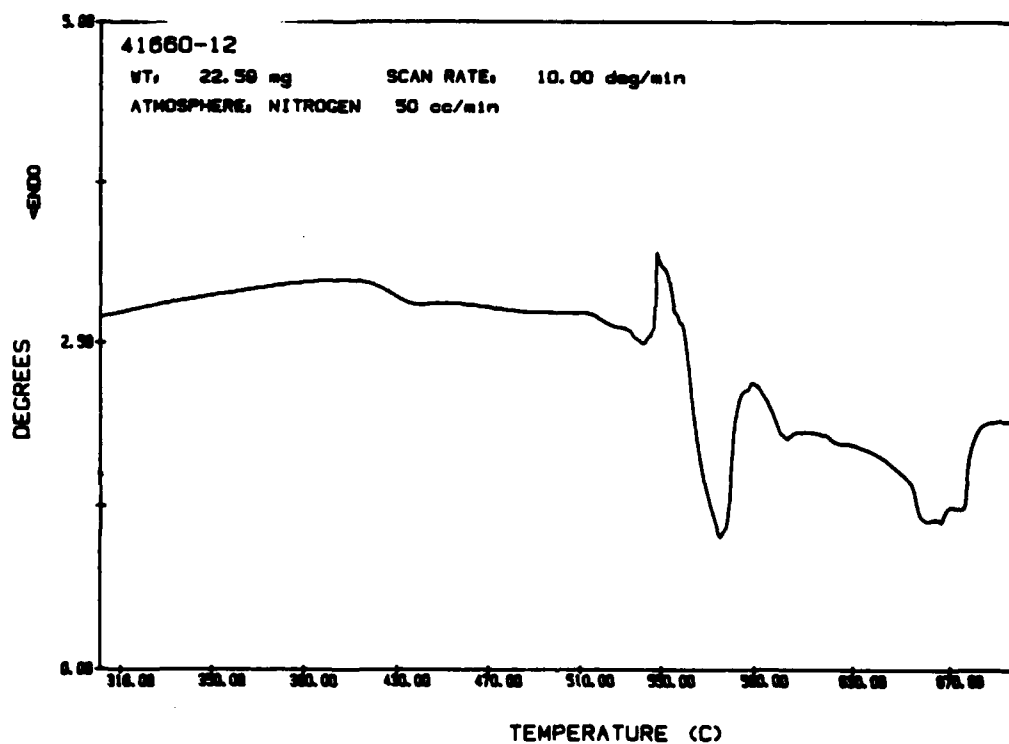
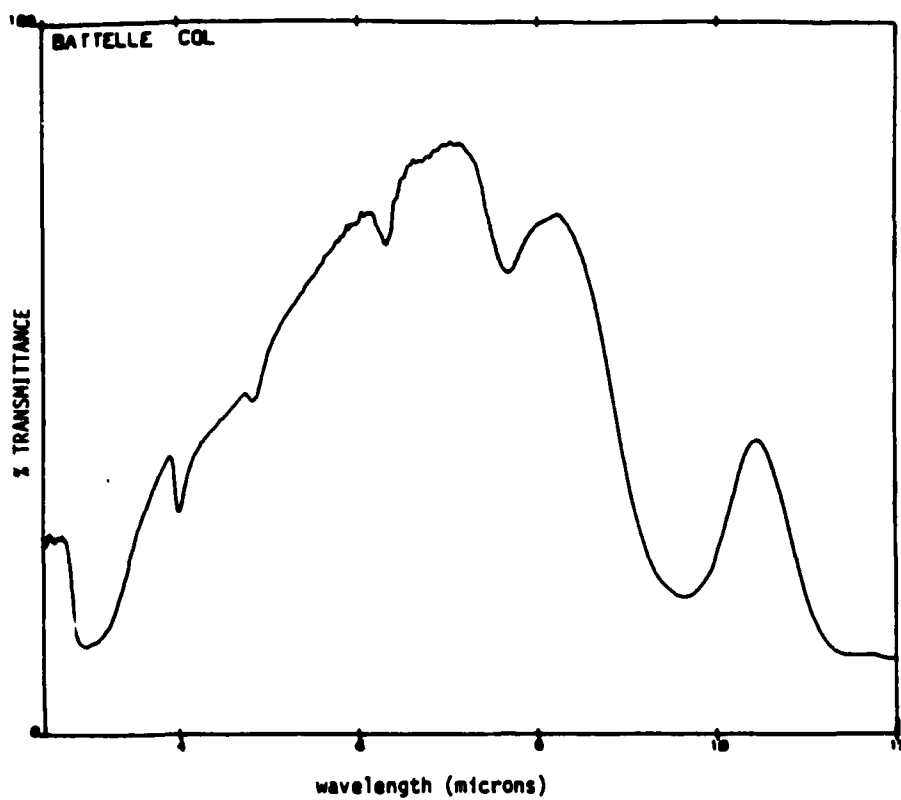


Figure 1. Rocking Furnace

FIGURE 2. SEM (1000X) OF  $\text{Ge}_{0.4}\text{P}_{0.4}\text{S}_{0.2}$  GLASSFIGURE 3. DTA OF  $\text{Ge}_{0.4}\text{P}_{0.4}\text{S}_{0.2}$  GLASS





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FIGURE 4. INFRA-RED SPECTRUM OF  $\text{GeGa}_{0.2}\text{S}_{1.9}$  GLASS

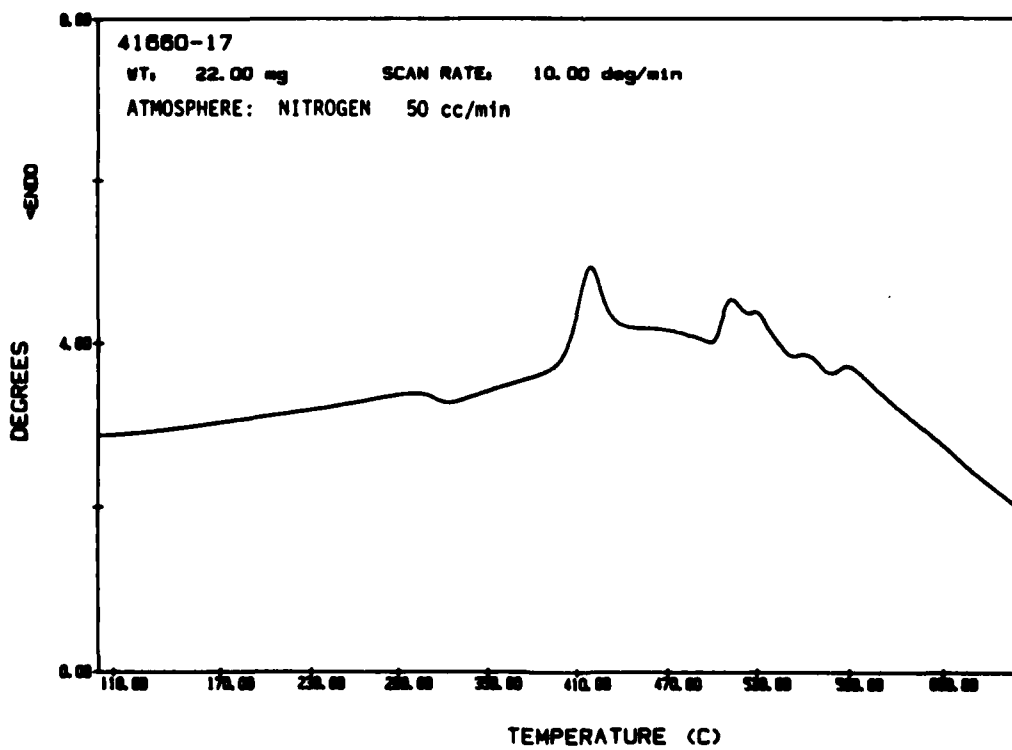


FIGURE 5. DTA OF  $\text{GeGa}_{0.2}\text{S}_{1.9}$  GLASS

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